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ENGLISH TRANSLATION DOCUMENT

The following attached document is the English Translation Document for the below referenced Chinese patent application.

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Title: Active Materials for the Positive Electrode of Anhydrous Rechargeable Batteries, Their Methods of Fabrication and Anhydrous Rechargeable Batteries Using Said Materials

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Attorney Docket: BYD-US2003-008

Translation Certification

I hereby certify that the following translation of the respective certified copy is

correct.



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Active Materials for the Positive Electrode of Anhydrous Rechargeable Batteries, Their
Methods of Fabrication and Anhydrous Rechargeable Batteries Using said Materials

Abstract

- 5 A type of active material for the positive electrode for anhydrous rechargeable batteries,
its method of fabrication and the use of said material in anhydrous rechargeable batteries.
The chemical formula for said active material for the positive electrode is
 $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ where $0.97 \leq a \leq 1.05$, $0.01 \leq b \leq 0.30$, $0 \leq c \leq 0.10$, and M is one or
more or the following: manganese, aluminum, titanium, chromium, magnesium, calcium,
10 vanadium, iron, and zirconium. It is made of small crystalline granules with average
granule diameter between $0.5\mu\text{m}$ and $4\mu\text{m}$ and whose volume is less than or equal to 10%
and secondary granules. Said material for the positive electrode is obtained by calcining
spherically shaped cobalt nickel hydroxy compound ($\text{Ni}_{1-b}\text{Co}_b(\text{OH})_2$) and compounds
containing lithium. This material for the positive electrode material have a higher tap
15 density such that anhydrous rechargeable batteries using said material for their positive
electrode have good discharge capacities, cycle properties, and large current discharge

characteristics.

Active Materials for the Positive Electrode of Anhydrous Rechargeable Batteries, Their
Methods of Fabrication and Anhydrous Rechargeable Batteries Using said Materials

Field of Invention

5 This invention relates to a type of active material for the positive electrodes of
anhydrous rechargeable batteries, its method of fabrication and anhydrous rechargeable
batteries using said material

Background of Invention

10 In recent years, with the widespread use of a variety of portable electronic
products, lithium ion rechargeable batteries with its many superior characteristics such as
high voltage, large specific capacity, low self-discharge, and zero memory effects, have
been highly favored. The positive material used in lithium batteries are mainly embedded
type compounds. At present, the material for the positive electrode with the best overall
15 properties is lithium cobalt material, LiCoO_2 .

However, the LiCoO_2 material is expensive and scarce. Therefore, people have

suggested using compounds of lithium manganese oxides or compounds of lithium nickel oxides as substitutes for the LiCoO_2 . Generally, doping or coating treatments are needed to overcome the deficiencies existing in the compounds of lithium manganese oxides and compounds of lithium nickel oxides. At present, the doping of the compounds of lithium manganese oxides and compounds of lithium nickel oxides to obtain the $\text{LiNi}_{1-b}\text{Co}_b\text{O}_2$ material has become the hotspot of people's research.

In preparing the $\text{LiNi}_{(1-b)}\text{Co}_b\text{O}_2$ material, people have generally use the calcination method on a mixture of compounds of lithium, nickel, and cobalt.

The article in Chen, Express, 6, 161191 provided a method to fabricate a type of $\text{LiNi}_{1-b}\text{Co}_b\text{O}_2$ material: mix together $\text{Ni}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2$ with LiOH solution.

Initially dry this mixture at 90°C , then heat treat at 800°C in air to produce the product.

Japan Patent Publications 2000-058053 discloses the composition method for a type of $\text{LiNi}_{1-b}\text{Co}_b\text{O}_2$ material. Calcine a predetermined ratio of a mixture of lithium, cobalt, and nickel salts in dried atmosphere without carbon dioxide at 300°C to 700°C for over 2 hours. Grind. Then calcine again at 700°C to 900°C to obtain the desired material.

Other than this, since, under higher temperature, the Ni^{3+} ion easily reverts back into the Ni^{2+} ion, people also first oxidizes the Ni^{2+} ion to become the Ni^{3+} ion, then calcine to react the mixture at lower temperatures to fabricate the $\text{LiNi}_{(1-b)}\text{Co}_b\text{O}_2$ material.

Chinese Patent Publications CN1142691A provides a method of heat treating at 400°C to 500°C the ingredients, oxides containing cobalt, hydroxide compounds of nickel, $\text{Ni}_{1-y}\text{Co}_y\text{OOH}$, and a type of lithium compounds, to fabricate the $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ material.

The $\text{LiNi}_{1-b}\text{Co}_b\text{O}_2$ material has a hexagonal layered structure. During its composition process, planar crystals are formed in the C axis direction such that it is easy to form crystals with uneven shapes. When using this type of uneven shaped crystals, conducting agents are needed to ensure electroconductivity thus making it difficult to increase filling density. In the alternative, the discharge capacity and large current discharge characteristics would be poorer. Also, the above mentioned methods require grinding in the treatment of the product resulting in minute crumbling granules, thus increasing the specific surface area of the material. In order to provide the electroconductivity, large quantities of conducting agent have to be added.

Therefore, the above method for the fabrication of the $\text{LiNi}_{1-b}\text{Co}_b\text{O}_2$ results in lower specific capacity for the material of the positive electrode due insufficient existing crystallization. It is also unfavorable in raising the filling density of the material thus resulting in raising the material's volume specific capacity or excessive conducting agent is needed to lower the specific capacity of the positive electrode of the rechargeable battery. Also, the large current discharge characteristics are poorer.

Description of Invention

This invention provides a type of active material for the positive electrode for anhydrous rechargeable batteries that possesses a higher tap density, its method of fabrication and the use of said material in anhydrous rechargeable batteries. This type of anhydrous rechargeable battery has good discharge capacity, cycle characteristics and large current discharging characteristics.

The object of this invention is implemented by the following technological plan:

The material for the positive electrode for a type of anhydrous rechargeable battery,

- (1) its chemical formula is: $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ ($0.97 \leq a \leq 1.05$, $0.01 \leq b \leq 0.30$, $0 \leq c \leq 0.10$, where M is one or more of the following: Mn, Al, Ti, Cr, M, Ca, V, and Fe; (2)

said material for the positive electrode is constituted of small crystalline granules and secondary granules formed by the aggregation of small crystalline granules. The granule diameter of the small crystalline granules is between $0.5\mu\text{m}$ and $4\mu\text{m}$ and the granule diameter of the secondary granules is between $10\mu\text{m}$ and $40\mu\text{m}$. Also the volume of the small crystalline granules is less than 10% of the total volume.

A further description of said secondary granules are that they are the $\text{Li}_{1-a}\text{Ni}_1\text{-b-cCo}_b\text{Mn}_c\text{O}_2$ crystalline granules formed during calcination by the mutual combination of small crystalline granules that continuously increase in size. They are either spherical or elliptical in shape.

The fabrication method for the active material of the positive electrode for anhydrous rechargeable batteries that includes the following steps:

(1) The fabrication of cobalt nickel hydroxy compound: add ammonia to a uniformly mixed solution of cobalt sulfate and nickel sulfate to form the cobalt nickel hydroxy compound, its structure is represented as $\text{Ni}_{1-b}\text{Co}_b(\text{OH})_2$.

(2) Compound of lithium nickel cobalt metal oxide:

(a) First calcination: Ballgrind and mix evenly predetermined quantities calculated from

the chemical formulae the following: lithium compound, said $\text{Ni}_{1-b}\text{Co}_b(\text{OH})_2$, and M

compound. Calcinate in oxygen atmosphere at between 600°C and 720°C for 1 hour to 10 hours;

(b) Second calcination: Calcinate the product from step (a) in oxygen atmosphere at

5 750°C to 900°C for 8 hours to 20 hours.

(c) Cool product from step (b) rapidly, ballgrind, sift to obtain the positive electrode material for said anhydrous rechargeable battery.

In step (1), control the shape of the cobalt nickel hydroxy compound

$\text{Ni}_{1-b}\text{Co}_b(\text{OH})_2$ to be either spherical or elliptical shaped with average granule diameter D_{50}

10 $\geq 8\mu\text{m}$, $D_{10} \geq 4\mu\text{m}$, and $D_{90} \leq 30\mu\text{m}$. The shape of the cobalt nickel hydroxy

compound is analyzed and observed with a scanning electron microscope, the granule

diameters D_{50} , D_{10} , and D_{90} is measured using the laser-scatter particle analyzer.

A preferred specification is in step 2(a), in order to compensate for the vaporization

during the high temperature calcination process, appropriate amounts of additional of

15 lithium compound should be used. In formulating the amounts of the reaction material

needed, the ratio of $\text{Li}/(\text{Ni}+\text{Co})$ should be ensured to be between 1.01 and 1.10.

The “b” in the structure of $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ is limited to be not greater than 0.3

because excess cobalt in the compound would lower the discharge specific capacity of the compound of lithium nickel cobalt metal oxide.

The average granule diameter of the secondary granules of the compound of

- 5 lithium nickel cobalt metal oxide is limited to between $10\mu\text{m}$ and $40\mu\text{m}$. The reasons are stated as follows. When the granule diameter is too small, a portion of the powder cannot be in contact with the conducting agent such that additional conducting agent must be used in order to ensure the conduction rate. In the alternative, when the average granule diameter is over $40\mu\text{m}$, the electrolyte cannot penetrate the inside of the granules
- 10 such that part of the material cannot be utilized during the charging and discharging reactions.

The reason for limiting compound of lithium nickel cobalt metal oxide to be spherical or elliptical shaped is to provide sufficient tap density. Moreover, uneven shapes are not favorable to the large current discharge characteristics of the active

15 material.

An anhydrous rechargeable battery, comprising of the following parts;

- (1) negative electrode, including lithium ion that can be attached and detached and/or metal lithium metal and/or lithium alloy as active material for the negative electrode;
- (2) positive electrode, including the active material for the positive electrode of claim 1 or 2; and
- 5 (3) electrolyte in contacting with said positive and negative electrode.

The advantages of this invention are as follows: By using suitable source material and controlling the specifications of its formation, the material that is obtained with the formula $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ and containing crystalline granules and secondary granules has higher tap density. Using said material for the material of the positive

10 electrode of batteries produces batteries with good discharge capacities, cycle properties, and large current discharge characteristics.

The following refers to the attached figures showing embodiments to explain this invention in further detail.

Figure 1 is the scanning electron micrograph of the cobalt nickel hydroxy

15 compound magnified 200 times.

Figure 2 is the scanning electron micrograph of the compound of lithium nickel

cobalt metal oxide of Embodiment 4 magnified 2000 times.

Figure 3 is the scanning electron micrograph of the compound of lithium nickel cobalt metal oxide of Embodiment 4 magnified 10,000 times.

Figure 4 is the diagram of the cross section of an embodiment in the form of a
5 button cell battery,

Implementation Modes

This invention provides the active material for the positive electrode for a type of anhydrous rechargeable battery. Its chemical formula is: $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ ($0.97 \leq a \leq 1.05$, $0.01 \leq b \leq 0.30$, $0 \leq c \leq 0.10$, where M is one or more of the following: Mn, Al, Ti, Cr, M, Ca, V, and Fe. Said material for the positive electrode is constituted of small
10 crystalline granules and secondary granules formed by the aggregation of small crystalline granules. The granule diameter of the small crystalline granules is between $0.5\mu\text{m}$ and $4\mu\text{m}$ and the granule diameter of the secondary granules is between $10\mu\text{m}$ and $40\mu\text{m}$. Also the volume of the small crystalline granules is less than 10% of the total
15 volume. This invention also provides the fabrication method for said active material for the positive electrode and an anhydrous rechargeable battery using said material.

In order to obtain material for the positive electrode where the metal ions are distributed evenly and reduce the redistribution during the combination reaction of nickel and cobalt. This invention uses the cobalt nickel hydroxy compound fabricated by adding ammonia to a uniformly mixed solution of cobalt sulfate and nickel sulfate. Its formula representation is $\text{Ni}_{1-b}\text{Co}_b(\text{OH})_2$. The advantage of using said cobalt nickel hydroxy compound is that the cobalt nickel hydroxy compound can be fabricated to be spherically or elliptically shaped as shown in Figure 1. The process of fabricating the $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ material does not destroy the spherical shapes and instead grows many crystallites as shown in Figure 2, spherical or elliptically shaped active material for the positive electrode can be obtained from the cobalt nickel hydroxy compound. In this way, controlling the shape and granule diameter of the needed material can be accomplished by controlling the shape and granule diameter of the cobalt nickel hydroxy compound.

The lithium compound used in the reaction can be compound such as lithium hydroxide, lithium oxide, lithium peroxy-oxide, lithium carbonate, and lithium nitrate.

From the standpoint of the cost, customarily, lithium carbonate is used.

Mix uniformly the cobalt nickel hydroxy compound and lithium compound in predetermined quantities. Calcine in two steps under high temperature. First calcine at 600°C to 720°C for 1 to 10 hours in a process to decompose the cobalt nickel hydroxy compound and to oxidize the Ni²⁺ ion. Then calcine again at 750°C to 900°C for 8 hours to 20 hours for the formation of the crystalline granules and secondary granules.

First the lithium ions from the decomposed lithium compound enter the inside of the cobalt nickel hydroxy compound sphere to form many $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ crystalline granules, i.e., primary granules whose average granule diameter is between 0.5μm and 4μm. These crystalline granules uses the cobalt nickel hydroxy compound as the center and join together and continuously grew inside it to form the secondary granules of $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ whose average granule diameter is between 10μm and 40μm, as shown in Figure 3. If the temperature in the second calcination is lower than 750°C or the calcination time is less than 8 hours, then the growth of the crystallite cannot be completed.

If the temperature of the calcination is greater the 900°C or the time of calcination is longer than 20 hours, then the crystallites have grown too big such that they extrude and cannot aggregate and join together to form secondary granules. It is desirable to have as

many secondary granules as possible as few crystalline granules as possible when the $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{Mn}_c\text{O}_2$ is used as the active material in positive electrodes. In practice, the volume of the crystalline granules that is less than or equal to 10% of the total volume of the material can be obtained. When American Honeywell Microtrac X100 testing equipment is used to test the distribution of granules in said active material of positive electrodes and $D_{10} \geq 6 \mu\text{m}$, then the system does not contain more than 10% by volume crystalline granules that have not been formed into secondary granules.

Since Ni^{3+} ion reverts back to Ni^{2+} ion at temperatures higher than 600°C , therefore, oxygen atmosphere is needed to control the progress of this reaction.

Experiments show that the calcination process should proceed in oxygen pressure of approximately 1 atmosphere.

In formulating the reaction mixture, in order to compensate for the volatilization during high temperature calcination, adequate amounts of lithium compound have to be added. However, since the reaction cannot be calcined at overly high temperatures or

overly long time periods, excessive amounts of lithium compound can lead to the existence of contamination in the product. Therefore in formulating the reaction material,

the ratio of Li/(Li+Co+M) should be ensured to be between 1.01 and 1.10.

$\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ has different structures at high and low temperatures.

Moreover, only the hexagonal layered halite structure at high temperature has

electrochemical properties. Therefore, rapid cooling is required to retain high

5 temperature phase structure of the product.

The following embodiments further explain this invention.

The first part: Embodiments relating to reaction specifications.

Ballgrind to mix the cobalt nickel hydroxy compound $\text{Ni}_{0.81}\text{Co}_{0.19}(\text{OH})_2$ that are

elliptical or spherical in shape with granule diameter between $8\mu\text{m}$ and $10\mu\text{m}$ and 5.2

10 times molar equivalent of lithium carbonate. Table 1 shows the different products with

different structures that are produced under varying conditions of calcination. The

different products from the embodiments with different structure are tested below and

made into batteries in the embodiments and comparison examples.

Powdered X-ray diffraction (Cu-K α) is used to determine the structure of the

15 product and to test whether there is lithium carbonate mixed in.

After the obtained product is sifted with 400 mesh with a guage of $38.5\mu\text{m}$, JEOL's

scanning electron microscope JSM-5610 tester is used to observe the shape and size of the secondary granules and the crystalline granules that forms the secondary granules at 2000 magnification and 10000 magnification.

American Honeywell Microtarc X-1000 analyzer, a granule diameter distribution analyzer, is used to document the value of D_{50} and D_{10} of the product.

100g of the product is placed in a slender long cylinder marked with even calibrations. The cylinder is then dropped to freefall from a height of 50cm onto a rubber floor for 100 times. The volume of the product is then read to calculate the tap density.

Dissolve polyvinylidene fluorine (PVDF) in N-methyl-pyrrolidone (NMP) at 120°C. Fully mix the dried material for the positive electrode, the compound of lithium nickel cobalt metal oxide compound, acetyline black (conducting agent), and the dissolved PVDF in the weight ratio of 85:10:5. Dry for over four hours to obtain the mixture of positive electrode material.

Battery properties are further explained using the button cell battery as an example.

15 Weigh and use 0.102g of the mixture of the material for the positive electrode.

Use nickel net with small pores that has been treated with hydrochloric acid and dried as

the current collector and form a disc with ϕ 13mm diameter at 10Mpa pressure. Place the disc in a vacuum furnace at 160°C for 4 hours and to disperse binder agent and form the required positive electrode slice of the battery.

As shown in Figure 3, in a glove box in Ar atmosphere, use the positive electrode slice 4, a lithium slice with surface oxide material and ϕ 16mm diameter as the negative electrode 2, a polyethylene multiple aperture membrane as the separator membrane 2, a positive electrode shell 6, a negative electrode shell 1, and an insulation gasket 5 to form button battery. The battery uses 1 mol./liter of lithium phosphate hexafluoride (LiPF_6) as the electrolyte agent, and, ethyl carbonate (Ec) and dimethyl carbonate (DMC) mixed in a predetermined weight ratio as the electrolyte solution.

The button cell battery can be tested 1 hour after fabrication. Charge battery with 1mA of current until the open circuit voltage reaches 4.2v. After setting aside for 30 minutes, discharge at 1mA until the open circuit voltage is 3.0 volts. The resulting discharge capacity is the initial discharge capacity. The initial specific discharge capacity is the (initial discharge capacity)/the weight of the positive material. Its units are mAh/g.

Use said discharge specifications to repeatedly charge and discharge battery.

After repeating 100 times, the 100 cycle capacity retention rate can be obtained by the following:

$$100 \text{ cycle capacity retention rate} = (\text{discharge capacity at the } 100^{\text{th}} \text{ discharge}) / (\text{initial discharge capacity}) * 100\%$$

Charge a new button cell battery that has never been charged or discharged with 1mA of current until the open circuit voltage reaches 4.2v. Set aside for 30 minutes then discharge battery with 1mA of current until the open circuit voltage reaches 3.0v to obtain the discharge capacity recorded as 1mA discharge capacity. Then charge battery with 1mA of current until the open circuit voltage reaches 4.2v. Set aside for 30 minutes.

Then discharge battery with 5mA of current until open circuit voltage reaches 3.0v. The resulting discharge capacity is recorded as the 5mA discharge capacity. The large current discharge characteristic can be obtained by the following:

$$\text{Large current discharge characteristic} = (5\text{mA discharge capacity}) / (1\text{mA discharge capacity}).$$

Tested and experimented using above-described specifications. Embodiment 1

through 5 and Comparison Examples 1 through 5 are tested according to the calcination

specification listed in Table 1. The results of the different tests are shown in Table 1.

Table 1 Embo- diment Number	First Calcina- tion Temp- erature (°C)/(h)	Second Calci- nation Temp- erature (°C)/(h)	Calci- nation Atmo- sphere	Lithium Carbonate Mixed In	Secon- dary Granules Shape/ Size (μ m)	Primary Granules Shape/ Size (μ m)	Granule Diameter Distribu- tion D50/D10 (μ m)	Tap Density (g/cm ³)
Embo- diment 1	600/8	750/20	Oxygen	No	Spherical /11.5	Spherical /2.0	11.8/6.8	2.45
Embo- diment 2	650/6	750/20	Oxygen	No	Spherical /11.5	Spherical /2.0	11.7/6.6	2.43
Embo- diment 3	700/1	800/16	Oxygen	No	Spherical /12.0	Spherical /2.5	12.0/6.6	2.52
Embo- diment 4	650/6	800/16	Oxygen	No	Spherical /12.0	Spherical /2.5	12.2/6.9	2.51
Embo- diment 5	650/6	850/12	Oxygen	No	Spherical /13.0	Spherical /3.0	12.9/6.5	2.48
Embo- diment 6	650/6	900/8	Oxygen	No	Spherical /14.0	Spherical /3.5	14.4/6.8	2.44
Compa- rison	500/10	800/16	Oxygen	No	Uneven /13.0	Uneven/ 3.0	13.3/7.0	2.10

Example 1								
Compa- rison Example 2	750/1	800/16	Oxygen	No	Uneven /11.0	Uneven /2.0	11.6/6.2	2.18
Compa- Rison Example 3	650/6	700/30	Oxygen	Yes	Spherical /10.0	Spherical /0.2	9.8/4.4	2.48
Compa- rison Example 4	650/6	1000/4	Oxygen	No	No	Spherical /5.5	5.2/2.8	1.89
Compa- rison Example 5	650/6	800/16	Air	Yes	Spherical with Burrs /10.0	Uneven /0.5	10.4/5.5	2.03

(C'td)	First	Second	Calcina-	Initial	100 Cycle	Large
Table 1	Calcina-	Calcina-	Tion	Discharge	Capacity	current
Embo-	Tion	Tion	Atmo-	Specific	Retention	Discharge
	Temp	Temp	sphere	Capacity	Rate(%)	Characte-

diment Number	-erature (°C)/(h)	-erature (°C)/(h)		(mAh/g)		ristics (%)
Embo- Diment 1	600/8	750/20	Oxygen	178	92.7	78.4
Embo- Diment 2	650/6	750/20	Oxygen	180	92.4	77.9
Embo- Diment 3	700/1	800/16	Oxygen	181	92.0	78.7
Embo- Diment 4	650/6	800/16	Oxygen	185	92.8	78.6
Embo- Diment 5	650/6	850/12	Oxygen	183	91.9	78.2
Embo- Diment 6	650/6	900/8	Oxygen	184	92.4	76.2
Comparison Example 1	500/10	800/16	Oxygen	176	85.4	50.3
Comparison Example 2	750/1	800/16	Oxygen	178	83.2	54.9
Comparison Example 3	650/6	700/30	Oxygen	156	71.9	56.7
Comparison	650/6	1000/4	Oxygen	182	86.4	45.1

Example 4						
Comparison Example 5	650/6	800/16	Air	160	77.0	60.4

The second part: relating Co content of embodiments.

Table 2 selected different values of b for the ingredients of $\text{Ni}_{1-b}\text{Co}_b(\text{OH})_2$. All

other specifications are as the same as Embodiment 4 for Embodiment 7 through 12 and

- 5 Comparison Examples 6 through 9. Properties such as shape, granule diameter and tap density are basically the same as Embodiment 4. Other test results are shown in Table 2.

Table 2 Embodiment Number	Level of b $\text{Ni}_{1-y}\text{Co}_y(\text{OH})_2$	Initial Discharge Specific Capacity (mAh/g)	100 Cycle Capacity Retention Rate (%)	Large current Discharge Characte- ristics (%)
Embodiment 7	0.01	192	85.5	64.5
Embodiment 8	0.05	190	87.8	73.3
Embodiment 9	0.10	187	91.2	77.4
Embodiment 10	0.19	185	92.8	78.6
Embodiment 11	0.25	180	92.7	78.6

Embodiment 12	0.30	175	93.1	78.9
Comparison 6	0	205	82.2	47.1
Comparison 7	0.35	170	93.5	79.2
Comparison 8	0.5	153	94.1	80.8
Comparison 9	1	145	95.4	82.0

The third part: relating to the comparison of the volume of the secondary granules and the crystalline granules of $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$

- Follow the first part of the fabrication method of Embodiment 4 to fabricate the
- 5 lithium nickel peroxi-oxide oxide compound positive electrode material.

Sift part of the positive electrode material and collect secondary granules that are larger than $8\mu\text{m}$ and label them as A.

Grind part of the positive electrode material with grinder until all secondary granules are broken into crystalline granules and label them as B.

- 10 Mix A and B according to the ratios listed in Table 3. Determine the granule diameter distribution and tap density Embodiments 13 and 15 and Comparison Examples 10 through 12. Also, make batteries following the fabrication method in Part 1. The results are shown in Table 3.

Table 3 Embo- diment Number	A : B (Volume Ration)	D10/ μm	Tap Density (g/cm ³)	Initial Discharge Specific Capacity (mAh/g)	100 Cycle Capacity Retention Rate (%)	Large current Discharge Characte- ristics (%)
Embo- diment 13	100 : 0	8.2	2.57	185	92.6	78.2
Embo- diment 14	95 : 5	8.0	2.54	186	92.9	78.8
Embo- diment 15	90 : 10	6.4	2.52	185	92.8	78.6
Compa- rison 10	85 : 15	3.4	2.29	172	93.0	74.3
Compa- rison 11	50 : 50	1.2	1.85	165	93.5	56.1
Compa- rison 12	0 : 100	0.5	1.60	157	93.6	53.7

It can be seen from the above table that, when the granule diameter distribution of said positive electrode material was tested, when D_{10} is greater than $6\mu\text{m}$, i.e., when the volume of the crystalline granules that did not form the secondary granules in the system

5 is less than 10%, the battery exhibit good electrical properties.

The third part: relating to the shape of the $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ in the embodiments.

For Comparison Example 13:

The composition method is the same as Embodiment 3. The difference is that

5 the cobalt nickel hydroxy compound $\text{Ni}_{0.81}\text{Co}_{0.19}(\text{OH})_2$ has uneven shapes and is between $8\mu\text{m}$ and $10\mu\text{m}$. The active material for the positive electrode, the compound of lithium nickel cobalt metal oxide that has been fabricated is analyzed with a scanning electron microscope and its tap density measured. Also, the button cell battery is fabricated according to the method in Part 1. Its initial discharge specific capacity and large current

10 discharge characteristics are tested. (Table 4)

Table 4 Embodiment Number	Shape of Secondary Balls	Tap Density (g/cm ³)	Initial Discharge Specific Capacity (mAh/g)	Large current Discharge Characte- ristics (%)
Embodiment 4	Spherical	2.51	185	78.6
Comparison 13	Plate Shaped,	2.09	178	60.4

	Tetrahedron Shaped; etc. Uneven Shaped			
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From the above Embodiments and Comparison Examples, it can be seen that, the positive electrode material, the compounds of lithium nickel cobalt oxide, fabricated by the method of this invention is constituted of secondary granules formed by the combination of crystalline granules. This secondary granules are spherical or elliptical

5 shaped and increase the tap density of the material for the positive electrode. At the same time, rechargeable batteries using said positive electrode material has higher discharge capacity, better charge and discharge cycle characteristics and large current discharge characteristics.

Claims

1. The material for the positive electrode for a type of anhydrous rechargeable battery,

its characteristics are:

(1) Its chemical formula is: $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$ ($0.97 \leq a \leq 1.05$, $0.01 \leq b \leq 0.30$, $0 \leq c$

5 ≤ 0.10 , where M is one or more of the following: Mn, Al, Ti, Cr, Mg, Ca, V, and Fe.

(2) Said material for the positive electrode is constituted of small crystalline granules and

secondary granules formed by the aggregation of small crystalline granules. The granule

diameter of the small crystalline granules is between 0.5 and 4 μm and the granule

diameter of the secondary granules is between 10 and 40 μm . Also the volume of the

10 small crystalline granules is less than 10% of the total volume.

2. The material for the positive electrode of a type of anhydrous rechargeable battery of

claim 1, its characteristics are: said secondary granules are the $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{M}_c\text{O}_2$

crystalline granules formed during the calcination by the mutual combination of small

crystalline granules that continuously increase in size.

15 3. The fabrication method for the material for the positive electrode of a type of

anhydrous rechargeable battery of claim 1 or 2, its characteristics are: this method includes

the following steps:

(1) The fabrication of cobalt nickel hydroxy compound: add ammonia to a uniformly mixed solution of cobalt sulfate and nickel sulfate to form the cobalt nickel hydroxy compound, its formula representation is $\text{Ni}_{1-b}\text{Co}_b(\text{OH})_2$ compound.

5 (2) Compounds of lithium nickel cobalt metal oxide:

(a) First calcination: Ballgrind and mix evenly predetermined quantities calculated from the chemical formulae the following: lithium compound, said $\text{Ni}_{1-b}\text{Co}_b(\text{OH})_2$, and M compound. Calcinate in oxygen atmosphere at between 600°C and 720°C for one hour to 10 hours;

10 (b) Second calcination: Calcinate the product from step (a) in oxygen atmosphere at between 750°C and 900°C for 8 to 20 hours.

(c) Cool product from step (b) rapidly, ballgrind, sift to obtain the positive electrode material for said anhydrous rechargeable battery.

4. The fabrication method for the material for the positive electrode of a type of

15 anhydrous rechargeable battery of claim 3, its characteristics are: In step (1), control the shape of the cobalt nickel hydroxy compound $\text{Ni}_{1-b}\text{Co}_b(\text{OH})_2$ to be either spherical or

elliptical shaped with average granule diameters $D_{50} \geq 8\mu\text{m}$, $D_{10} \geq 4\mu\text{m}$, and $D_{90} \leq 30\mu\text{m}$.

5. The fabrication method for the material for the positive electrode of the anhydrous rechargeable battery of claim 3, its characteristics are: in step 2(a), the ratio of

5 $\text{Li}/(\text{Ni}+\text{Co}+\text{M})$ is between 1.01 and 1.10.

6. An anhydrous rechargeable battery, comprising of the following parts;

(1) negative electrode, including lithium ion that can be attached and detached and/or metal lithium metal and/or lithium alloy as active material for the negative electrode;

(2) positive electrode, including the active material for the positive electrode of claim 1 or

10 2;

(3) electrolyte in contacting with said positive and negative electrode.

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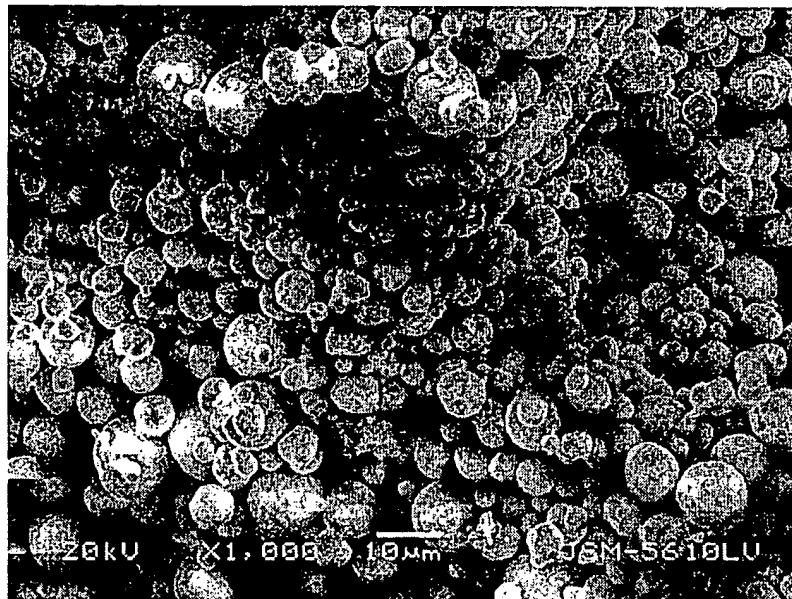


Figure 1

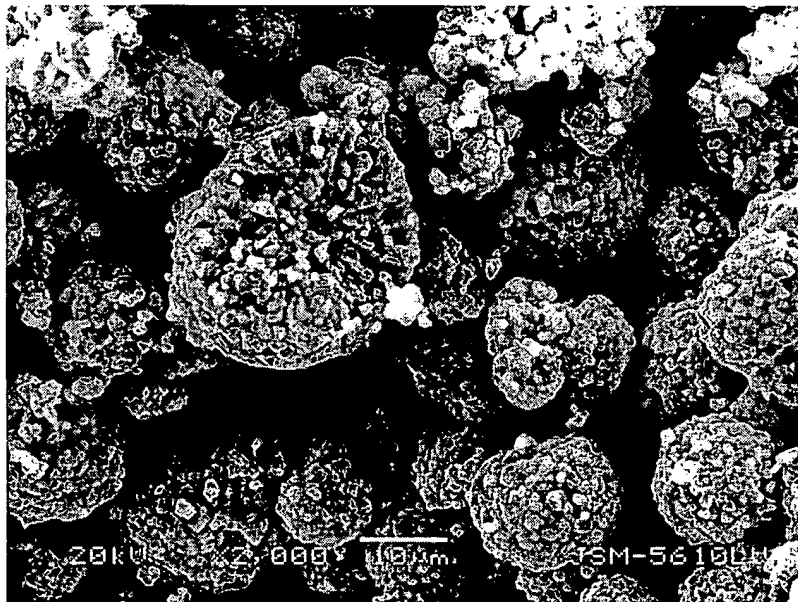


Figure 2

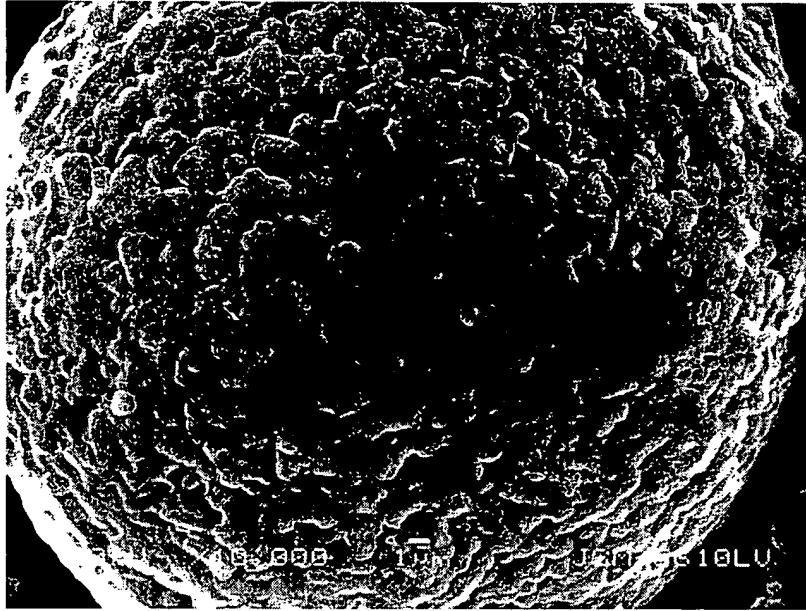


Figure 3

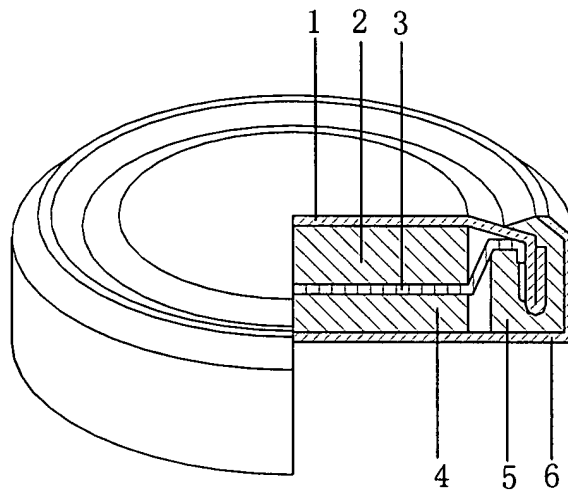


Figure 4